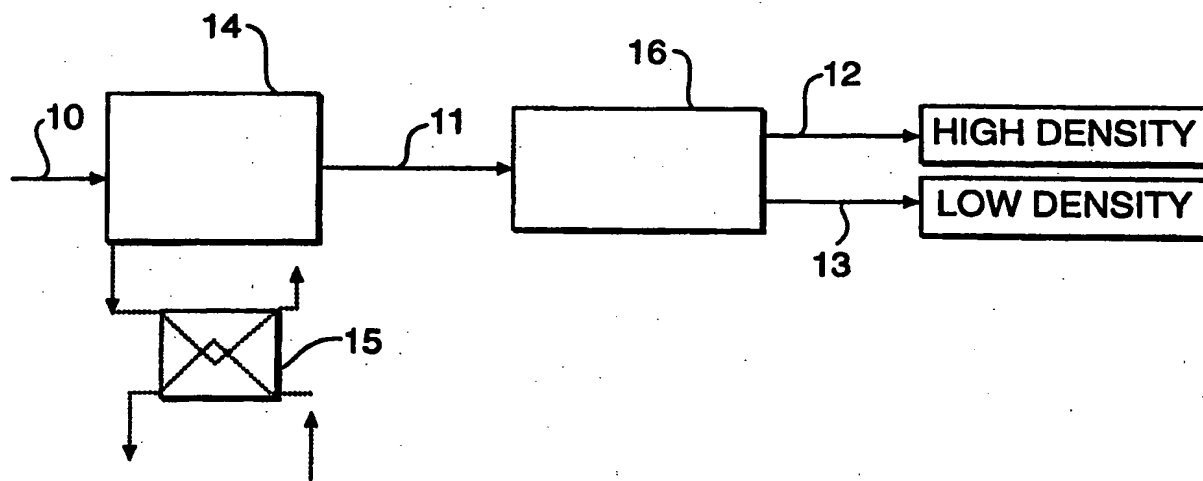




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<b>(21) International Application Number:</b> PCT/US98/06400 <b>(22) International Filing Date:</b> 31 March 1998 (31.03.98) <b>(30) Priority Data:</b> 08/831,337      31 March 1997 (31.03.97)      US <b>(71) Applicant:</b> WATERWORKS INTERNATIONAL, INC. [US/US]; 130 Commerce Way, Woburn, MA 01801 (US). <b>(72) Inventors:</b> CONANT, Lawrence, D.; 57 Grant Street, West Bridgewater, MA 02379 (US). KEUS, Arie; 66 Manning Road, Lynn, MA 01902 (US). <b>(74) Agents:</b> MEYER, Richard, S. et al.; Morgan Lewis & Bockius LLP, 1800 M Street, N.W., Washington, DC 20036-5869 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published:</b> <i>Without international search report and to be republished          upon receipt of that report.</i>

**(54) Title:** SULFURIC ACID PURIFICATION PROCESS**(57) Abstract**

A process for purifying an aqueous sulfuric acid solution includes cooling an aqueous sulfuric acid solution to at or near its freezing point to form a slurry of a solid phase and a liquid phase. The slurry has an acid-rich region and an acid-poor region. The acid-rich region is separated from the acid-poor region on the basis of density.

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## **SULFURIC ACID PURIFICATION PROCESS**

### **Field of the Invention**

The invention relates generally to a process for purifying a sulfuric acid solution, and more particularly, to a freeze concentration method of purifying an aqueous sulfuric acid solution by cooling the aqueous sulfuric acid solution to a temperature at or near its freezing point and separating the resulting acid-rich region from the acid-poor region.

### **Background of the Invention**

The treatment and disposal of spent industrial process waste waters, particularly acid-containing waste waters, has been a long standing problem in many industries. Acid-containing waste waters, also known as spent acid streams, are by-products of numerous manufacturing and refining processes. Increasingly higher disposal costs and numerous environmental issues connected with "hazardous" waste disposal have accentuated the need to treat acid-containing waste waters. For example, many local municipalities are enacting measures designed to encourage industrial waste water generators to seek alternative methods of treatment that do not rely on traditional neutralization and landfill practices. The pressure for new treatment methods is also enhanced by the diminishing amounts of landfill space capable of handling spent industrial waste water, and acid-containing waste water in particular.

Sulfuric acid is, by far, one of the most widely used chemicals in industrial chemistry. Annually, sulfuric acid production in the United States exceeds 48 million tons. Sulfuric acid is used, for example, in etching processes, in electroplating processes, in fertilizers, in catalysis, as well as a reagent for chemical synthesis. From such uses, one-third, or up to 16 million tons per year of sulfuric acid must be disposed of as an acid-containing waste. Current disposal methods are inadequate to met this need, involve costly technologies, and/or generate additional waste to be disposed.

Neutralization is the most popular method of waste sulfuric acid solutions. To neutralize sulfuric acid, a variety of bases are added to a sulfuric acid wastewater stream until the stream has been totally neutralized. A considerable drawback to this process is that for every ton of acid, four tons of base are generally required. Thus, for every ton of sulfuric acid, neutralization disposal techniques produce five tons of waste generally requiring landfill disposal.

Reverse osmosis has also been used to treat or dispose of sulfuric acid. Reverse osmosis forces waste sulfuric acid through costly filtration systems until the acid content of the stream is reduced to a level where the remaining stream can be disposed of by conventional means. This requires an expensive filtration system which is generally difficult to build and maintain. Moreover, current reverse osmosis filtration systems are only effective for treating small volume streams.

Evaporation represents another possible disposal method to treat sulfuric acid-containing wastes. However, to dissipate or remove water from an aqueous sulfuric acid solution requires significant energy input and, therefore, carries a high cost.

Incineration may be also used to dispose of waste sulfuric acid. Like evaporation, incineration is not expensive but may lead to the creation of acid rain. The possibility of acid rain makes incineration environmentally unacceptable.

As a result of the limitations in current disposal methods, there exists a need for a cost effective and environmentally prudent method to treat and/or dispose of waste sulfuric acid. A further need exists to reduce the amount of sulfuric acid-containing waste requiring ultimate disposal in a landfill. A preferable answer to this need would be to recycle spent sulfuric acid streams such that they may be reused. Recycling sulfuric acid would also answer and reduce the need for landfill disposal. While many sulfuric acid recycling processes have been proposed in the past (see, e.g., U.S. Patents 4,163,047, 4,954,322,

5,275,701 and 5,228,885) to date, there has been no commercially feasible process to recycle spent sulfuric acid streams.

### Summary of the Invention

The invention answers the problems arising from sulfuric acid disposal by providing a cost effective and environmentally prudent method of purifying an aqueous industrial sulfuric acid solution to produce a reusable acid product. The method of the invention is particularly useful with aqueous solutions of sulfuric acid which are formed as by-products of industrial processes. By purifying an aqueous sulfuric acid solution, the invention recycles sulfuric acid for consumption and reduces the amount of sulfuric acid waste requiring disposal.

More specifically, the invention provides a method of purifying, or enriching, an aqueous sulfuric acid solution through the use of a freeze crystallization process in which an aqueous sulfuric acid solution is cooled to a temperature at or near its freezing point to form a slurry of a solid phase and a liquid phase. This cooled slurry mixture contains an acid-rich region and an acid-poor region which are subsequently separated on the basis of density. The sulfuric acid concentration in the aqueous sulfuric acid solution typically ranges from 10-95% by weight. The aqueous sulfuric acid solutions may also contain acids other than sulfuric acid, such as nitric and hydrochloric acid. By purifying the aqueous sulfuric acid solution, impurities contained in the solution may be removed and the concentration of the sulfuric acid may be increased, to levels sufficient for recycling and reuse.

Various processes and apparatus for carrying out the purification process are contemplated but the freeze concentration apparatus disclosed in the assignee's U.S. Patent No. 5,394,706 is preferred. The cooling of the aqueous sulfuric acid solution may occur in a conventional heat exchanger. One embodiment of the invention separates the acid-rich region from the acid-poor region on the basis of density in a density column. In another embodiment of the invention, the separation occurs by centrifuging the cooled slurry to

separate the acid-rich region from the acid-poor region. In a further embodiment, the separation step involves sequentially feeding the solid-liquid phase slurry through a combination of a density column and a centrifuge and separating the acid-rich region from the acid-poor region on the basis of density. Another embodiment of the invention employs the cooled, separated, acid-rich region and/or acid-poor region to precool an aqueous sulfuric acid solution entering the method to be purified. The method of the invention may be a continuous or batch process. In a continuous process, a portion of the separated acid-rich region or the separated acid-poor region may be mixed with the initial aqueous sulfuric acid solution in order to control the sulfuric acid concentration of the solution to be purified.

Other advantages and features of the invention will be apparent from consideration of the detailed description of the invention provided below.

#### Brief Description of the Drawings

FIG. 1 is a sample of phase diagram for a binary mixture.

FIG. 2 is a phase diagram for sulfuric acid in water. Taken from Gable, Eetz & Maron, JACS, vol. 72, 1446-1448 (1960).

FIG. 3 is a schematic flow diagram illustrating the freeze concentration process of the invention.

#### Detailed Description of the Preferred Embodiments

The invention provides a commercially feasible method of purifying an aqueous sulfuric acid solution on a large commercial scale. The method may be used with any sulfuric acid solution having impurities but is particularly useful for aqueous sulfuric acid solutions resulting from industrial processes. Such solutions contain not only sulfuric acid but other by-products from the particular process. The method of the invention may remove the impurities, purify the aqueous sulfuric acid, and permit its reuse in the same or a different process. To purify an aqueous sulfuric acid solution, the method cools an aqueous sulfuric acid solution to at or near its freezing point to form a slurry of a solid phase and a liquid

phase. The cooled mixture contains an acid-rich region and an acid-poor region. The method separates the acid-rich region from the acid-poor region on the basis of their different densities.

The invention takes advantage of the relationship between the solid and liquid phases of a mixture of two components--sulfuric acid dissolved in water. When a solute, such as sulfuric acid, is dissolved in another substance, such as water, the temperature at which the liquid composition becomes a solid depends, not only upon temperature, but also upon the concentration of the system. This relationship may be depicted using a phase diagram such as in Figure 1, which shows a typical phase diagram for a mixture of a binary solution of compounds A and B. The phase diagram consists of a horizontal axis of weight percent of one component and a vertical axis of temperature. The normal shape of the relationship of the solid and liquid phases is depicted by a curve that shows decreasing temperature with increasing concentration to a point called the "eutectic point." At concentrations higher than the eutectic point, the curve rises in temperature with increasing concentration. This curve is called the "saturation curve." In other words, the curve represents the highest concentration of A for a saturated solution at a given temperature. A change in temperature, for example pushing below the saturation curve, results in a change in concentration.

In the solid-liquid phase diagram of Figure 1, M is the melting point of pure B and P is the melting point of pure A. The curves MFHU and PDU represent the solubilities of components B and A, respectively, in their liquid solution. For example, a liquid solution at point E, if cooled, precipitates B, so the solution becomes richer in A. At point G, the liquid and solid A are in equilibrium at a temperature corresponding to points F and G. As the temperature is lowered below point F, additional B precipitates (represented as point I), while the concentration or weight fraction of component A in the liquid composition gradually increases, which is represented on the diagram by moving along the curve FHU through point H and toward U. The point U represents the eutectic point for the mixture of A and B. If the

temperature is further lowered to a point corresponding to U, the liquid remaining is a eutectic mixture, and any further cooling results in complete solidification of a mixture of A and B without a change in concentration. This solid is called the eutectic solid. Similarly, if the liquid solution was originally at C and cooled to D, the solid precipitating would be A. Further cooling at this condition will result in pure A until the eutectic point U is reached.

As shown by the phase diagram in Figure 1, a saturated solution, when cooled, preferentially precipitates one component, the solute, as the solution changes in concentration toward the eutectic point. In general, the component precipitates in its pure form as crystals. As they form, the crystals exclude other impurities present in the original solution. Collecting the crystals, then, provides a means for obtaining a purified product. Freeze concentration systems and methods like the invention operate by taking advantage of this principle.

In the case of a simple binary system, the solid phase, in theory, does not contain any solvent when the composition of liquid which is partially frozen is on either side of the eutectic composition. In practice, it is very difficult to attain this condition, and often the solid phase A does contain B because of volumetric inclusions. Also, there may be slight solid solubility in the ultrapure region.

As shown by the solid-liquid phase diagram in Figure 2, an aqueous solution of sulfuric acid differs significantly from a simple binary system, such as shown in Figure 1. Sulfuric acid is the nonvolatile product of the reaction of sulfur trioxide ( $\text{SO}_3$ ) and water ( $\text{H}_2\text{O}$ ). By convention, mixtures of sulfur trioxide and water are expressed as percent sulfuric acid. An aqueous solution of sulfuric acid forms several eutectic points and displays a complicated phase diagram. This is due at least in part to the ability of sulfuric acid to form hydrates with water. For example, sulfuric acid with water can form a monohydrate,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , a dihydrate,  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , a trihydrate,  $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  and a tetrahydrate,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ . The freezing point for sulfuric acid concentrations between 0% and 38% by



weight varies from 32°F to -100°F. For sulfuric acid concentrations varying between about 38% to 74% by weight the freezing point is less than -20°F. Interestingly, the freezing point for sulfuric acid concentrations ranging from about 74% to 94% by weight varies from a low of about -32 °F to a high of about 48°F. The sulfuric acid concentration region of from about 94% to 100% by weight has a freezing point temperature range of from about -32°F to about 50°F.

The method of this invention applies principles such as those just discussed to purify an aqueous solution of sulfuric acid. The method cools an aqueous sulfuric acid solution to at or near its freezing point to create a solid-liquid slurry having an acid-rich region and an acid-poor region. The acid-rich region and acid-poor region may then be separated on the basis of density. The acid-rich region generally possesses a higher density than the acid-poor region.

The inventive method of purifying aqueous sulfuric acid may be used with any aqueous sulfuric acid solution. Of particular interest are aqueous sulfuric acid concentrations ranging from about 10-95% by weight, preferably about 20-95% by weight and most preferably about 74-95% by weight. The solution may contain other acids, such as nitric acid or hydrochloric acid, in combination with the sulfuric acid solution. Such mixed acid solutions are often used in industrial processes or formed as a by-product. When other acids are present in combination with sulfuric acid, the combined total acid concentration generally will range from about 10-50% by weight, more preferably about 10-40% by weight and most preferably 10-30% by weight.

The aqueous sulfuric acid solution may contain impurities resulting from the process giving rise to the solution itself. Impurities for the purpose of the invention are defined as compounds other than water, sulfuric acid or hydrates of sulfuric acid, or other acids if the sulfuric acid solution is a mixed acid solution. Typical impurities include organics, organometallics and metals, including the salts and oxides of metals. Possible organic

impurities include oils, surfactants, resins and plastic residues. Typical metal impurities include sodium, lithium and heavy metals such as iron, copper, lead, chromium. By practicing the method of the invention, such impurities contained in the aqueous solution may be removed and the aqueous sulfuric acid purified. Because the method of the invention separates an acid-rich region from and acid-poor region, the method advantageously may also increase the concentration of the sulfuric acid in the aqueous sulfuric acid solution product. Using the method of the invention the sulfuric acid concentration may be increased, or enriched, by recovering the acid-rich region, for example up to 15%. Typical methods of the invention enrich the sulfuric acid concentration in an amount of from 0.01-10%.

The method of the invention will now be described by referring to an aqueous sulfuric acid purification system of the invention as shown in schematic form in Figure 3. Ancillary equipment, such as pumps, valves and the like, which may be necessary for operation of the system but which are not needed to explain the principles of the invention have not been shown nor described for purposes of clarity. It will be recognized by those skilled in the art that such ancillary equipment would, of course, be used in combination with the method and apparatus to practice the invention.

In the invention, the aqueous sulfuric acid solution is cooled to a temperature at or near its freezing point to form a solid-liquid slurry. The cooling step requires that the aqueous sulfuric acid be delivered, for example by means of a conduit 10, to an appropriate heat exchanger 14. The sulfuric acid solution is preferably free of solids prior to entering the heat exchanger 14. Inside the heat exchanger 14 the sulfuric acid solution is cooled such that a portion of the sulfuric acid solution forms a solid phase. In order to form such a solid phase, the sulfuric acid solution is cooled to at or near its freezing point. However, care must be taken such that only a portion of the aqueous sulfuric acid solution is cooled to form a solid crystalline material, hereinafter referred to as the solid phase. As mentioned above, upon formation the solid phase will exclude dissolved organic and inorganic impurities.

The solid phase formed in the heat exchanger 14 remains in contact with the liquid phase such that a solid-liquid slurry is formed having an acid-rich region and an acid-poor region. An acid-rich region is defined as a portion of the solid-liquid slurry that will separate on the basis of density to form a region having a higher sulfuric acid content than the remaining solid-liquid slurry. Depending on the sulfuric acid concentration of the initial aqueous sulfuric acid solution, the acid-rich region may be either the solid phase or liquid phase. Likewise, depending on the initial sulfuric acid concentration, the acid-poor region may be either the solid or liquid phase. Typically, the solid phase will contain sulfuric acid alone or in a hydrated form and will be the acid-rich region. The acid-rich region is also the higher density portion of the slurry.

A particularly preferred heat exchanger 14 for use in the invention is a scraped-surface freeze crystallizer described by the assignee's U.S. Patent No. 5,394,706, the disclosure of which is incorporated by reference herein. The scraped-surface crystallizer of this patent produces, removes, and pumps ice crystals in an economical and energy efficient manner. The main body of the crystallizer is made from an outer shell, a tube sheet on the feed or product inlet side, a tube sheet on the slurry discharge side, and a plurality of tubes disposed inside the shell and having ends supported by the tube sheets. The inner surface of the plurality of tubes are polished to facilitate ice scrapping and slurry flow. Positioned axially within each tube is a rod which is connected to a shaft at one end and a scraper at the other. The scraper is designed such that the flow of ice crystals through the tube is not impeded. The shaft is connected to a conventional drive motor, piston or other mechanism that imparts a back-and-forth or reciprocal motion to the shaft, rod and scraper.

However, any heat exchanger capable of cooling a feed stream to at or near its freeze point may be used in a method of the invention. The heat exchanger, is supplied with a suitable refrigerant at a temperature and flow rate such that a portion of the aqueous sulfuric acid freezes to form a solid phase. While the desired temperature of the refrigerant will

depend upon the nature and concentration of the aqueous sulfuric acid stream, generally the refrigerant temperature will be about -40 °F or higher, preferably about -30 °F or higher.

Any conventional refrigeration means 15 may be used to cool the heat exchanger. One such refrigeration means for the heat exchanger is a brine solution passed between a series of bundled tubes disposed within the shell of the heat exchanger as disclosed in U.S. Patent No. 5,394,706. However, no matter which particular type of heat exchanger and refrigerant is used, the temperature conditions in the heat exchanger depend upon the concentration of the aqueous sulfuric acid stream and its corresponding freezing point.

In order to properly control the crystallization process, the heat exchanger 14 will preferably contain devices capable of monitoring and controlling the cooling process. Thus, the heat exchanger may contain a differential temperature gauge across the crystallizer, and a pressure measuring device. By properly monitoring the cooling process, the refrigerant flowing through the heat exchanger can be varied to prevent the contents of the crystallizer from completely solidifying. Should the sulfuric acid feed stream completely solidify the heat exchanger should be shut down and thawed.

Another method of cooling the aqueous sulfuric acid solution is by direct injection of one or more refrigerants into the solution. However, this method of cooling is not preferred as it requires the refrigerant to be removed at a later stage, for example by evaporation. Cooling the solution to its triple point in a multistage flash evaporator may also be used. However, working at the triple point is not generally preferred due to the inherent difficulties in maintaining the solution at its triple point.

When the heat exchanger 14 is the preferred scraped-surface crystallizer, the aqueous sulfuric acid solution is conducted through the tubes where it is cooled and a solid phase forms on the interior of the tubes. The motion of the scraper causes the solid phase to be removed or scraped from the tube surface mixing with the liquid phase to form a solid-liquid slurry. The solid-liquid slurry, formed in the crystallizer, contains an acid-rich region and an

acid-poor region. This slurry is pumped out from the crystallizer and into a separator 16 via conduit line 11.

In the separator 16, the acid-rich region and acid-poor regions are separated on the basis of their differing density with the acid-rich region generally having the greater density. Generally, both the acid-rich region and the acid-poor region will both contain some solid and liquid phase material. Typically, for higher initial sulfuric acid concentrations, the sulfuric acid-rich region will have a larger amount of the denser solid phase and the sulfuric acid-poor region a larger amount of the lighter liquid phase. If the slurry contains a large amount of the solid phase, a portion of the solid phase may be melted to wash the remaining solid phase, to improve flow, or to free trapped or entrained impurities.

Separating the acid-rich region from the acid-poor region may be accomplished with any conventional density separation apparatus. Preferably, the separation occurs in a density column, a centrifuge, or in a sequential combination of the two.

When the separator 16 is a dynamic density column, the aqueous sulfuric acid solid-liquid slurry, containing an acid-rich region and an acid-poor region is generally conducted via line 11 to the mid-section of the density column. For a static density column the slurry is generally conducted to the top of the density column. A density column is a gradient device, with higher density materials settling toward the bottom of the device and lower density materials rising to the top. The density column may be of any conventional design known in the art. A preferred dynamic density column is the wash column described in U.S. Patent No. 5,394,706. A preferred density column contains pin mixing rods allowing easier separation of the solid-liquid slurry into at least one acid-rich region and at least one acid-poor region. If a density column having pin mixing rods is utilized, the rate of rotation of the pin mixing rods must be known and controlled.

Referring to Figure 3 and density column (separator 16), the aqueous sulfuric acid solid-liquid slurry enters the density column and remains for a time sufficient to allow

separation on the basis of density. Depending upon the initial concentration of the aqueous sulfuric acid solution, the higher density material may be either the acid-rich region or the acid-poor region. The higher density portion of the slurry is removed as "bottoms" from the density column through line 12 and lower density portion as "overheads" through line 13. The time spent in the density column is known as the "residence time." Given enough time the various concentrations of the acid-rich region and acid-poor region will return to the initial liquid aqueous sulfuric acid solution. Additionally, some of the frozen solid phase may be returned to a liquid phase due to the heat generated by mixing the various concentrations of sulfuric acid. This may increase the possibility of returning to the initial homogeneous concentration. However, the poor heat transfer characteristics inherent in a solid-liquid slurry works against this liquefaction. If the heat of mixing is deemed unacceptably high, which may occur in large density columns, cooling jackets may be used to remove excess heat. Thus, the residence time should be long enough to allow separation based on density but not so long as to permit the slurry to revert back to the initial liquid aqueous sulfuric acid solution. While the residence time is generally dependent upon the size and type of density column used, residence times will generally range from about 1 to 60 minutes, preferably about 2 to 30 minutes and most preferably 2 to 10 minutes.

The rate of separation and residence time in the density column will depend upon the relative upward and downward velocities of the acid-rich region and acid-poor region. The rate of downward velocity is increased by the removal rate of the higher density material from the bottom of the column and is decreased by an increased rate of slurry fed into the column.

Specific gravity may be measured to insure that proper separation is achieved. Specific gravity may be monitored manually on a periodic basis.

The temperature of the top and bottom discharge streams should be monitored to insure sufficient separation. Warmer temperatures favor a return to the initial homogenous

aqueous sulfuric acid solution as opposed to maintaining separate acid-rich and acid-poor regions.

Another method separating the acid-rich region from the acid-poor region involves the use of a centrifuge as the separator 16. A preferred centrifuge is the rotatable drum separator described in U.S. Patent No. 5,394,706, which separates a high density material from a low density material by means of two or more drums rotating at different speeds. The first rotatable drum is connected to one end of a hollow drive shaft and may have an approximate length to diameter ratio of 1:1. A second drum is mounted adjacent to the rotatable drum on the opposite side of the hollow drive shaft. The second drum may have a length-to-diameter ratio of approximately 1:10. The insider diameter of the two drums should be equal. The interiors of the drums are separated by a wall which extends radially inward from the second drum. The wall is perforated by a series of small holes in its outer periphery that allow a higher density phase to flow from the interior of the rotatable drum into the interior of the second drum. The wall has a central opening which may have a diameter equal to about one-half of the diameter of the rotatable drum. An auger is located inside the rotatable drum. When the rotatable drum is rotated, the auger is designed to rotate at a different speed, thereby providing for a scrapping motion by the auger. While the residence time in the centrifuge is highly dependent upon the size and type of centrifuge used, residence times will generally range from about 1 to 60 minutes, preferably about 2 to 30 minutes and most preferably 2 to 10 minutes.

When this type of separation apparatus is used, the aqueous sulfuric acid solid-liquid slurry is conducted via line 11 into the rotatable drum of the separator 16. Once inside the rotatable drum the rotation of the rotatable drum and auger causes a centrifugal effect to be produced. Due to the density differences between the acid-poor region and acid-rich regions of the slurry, the higher density material will be conducted through the small holes into the second drum. Depending upon the sulfuric acid concentration of the initial aqueous sulfuric

acid solution, the higher density material may be either the acid-rich region or the acid-poor region. A stationary tube located in the second drum allows the higher density material to be conducted out of the second drum. The higher density material is pumped through the stationary tube and into line 12. The motion of the auger in the rotatable drum removes the lower density material and any remaining higher density material from the rotatable drum exiting the centrifuge via line 13.

As discussed above, the acid-rich region may be separated from the acid-poor region using a density column or a centrifuge. Another embodiment of the invention uses a sequential combination of the two in either order. Combining a centrifuge with a density column achieves a higher degree of sulfuric acid purification. When employing both a centrifuge and a density column, the aqueous sulfuric acid solid-liquid slurry exits the heat exchanger to first enter the density column to separate and remove at least a portion of the acid-rich region. The remaining slurry may then be conducted to the centrifuge for further separation. It is also possible to purify the aqueous sulfuric acid by a first separation in the centrifuge followed by a subsequent separation in the density column. Through the use of a density column or centrifuge or both, separation can occur without the need of additional screening or filtration steps used in conventional processes.

Depending upon the nature of the aqueous sulfuric acid solution, it may be desirable to precool the aqueous sulfuric acid solution to a temperature above its freezing point. A cool stream (e.g., the acid-rich or acid-poor region removed from the density column or centrifuge) may be used as the refrigerant to precool the aqueous sulfuric acid solution prior to conducting the solution to the heat exchanger. A precooling heat exchanger may be used to precool the incoming aqueous sulfuric acid solution before the solution enters the heat exchanger to be cooled to form the solid and liquid phase. When the incoming aqueous sulfuric acid solution is precooled, it is possible for some contaminants to precipitate as solids which may be removed by nanofiltration, carbon absorption, ion exchange or other



techniques known in the art. Due to the corrosive nature of concentrated sulfuric acid streams, the stream may be diluted with water before precooling and removing any contaminant. Once the contaminant is removed to an acceptable level, the aqueous sulfuric acid may be reconcentrated using the method of the invention.

The sulfuric acid freeze concentration method of the invention may be used separately or in combination with other purification apparatus or processes. The method may be part of an industrial process to purify and recycle sulfuric acid solutions produced as a by-product of the process. Alternatively, the method may be used to purify and recycle aqueous sulfuric acid wastes as a stand alone process. Maximum benefits of the invention may be obtained when the method is practiced as a single pass process, using an apparatus such as that described and shown in Figure 1 of U.S. Patent 5,394,706.

The sulfuric acid purification process may be classified as batch, continuous or semibatch. The purification process may also be carried out as a continuous, steady state process. In a preferred process, the incoming and outgoing solutions are allowed to flow continuously through the method. Such a continuous process preferably uses a sequential combination of a centrifuge and a density column or of a density column and a centrifuge. When the method of the invention is practiced as a continuous process, a portion of the denser, generally acid-rich stream or, alternatively, the lighter, generally acid-poor stream may be cycled back and combined with the initial aqueous sulfuric acid solution. The stream cycled back to and mixed with the initial aqueous sulfuric acid may be taken from the centrifuge, the density column, or both. Cycling back a portion of the acid-rich or acid-poor region allows the method to be operated within concentration ranges which form the solid and liquid phases of the slurry at a particular operating temperature. Mixing of the acid-rich or acid-poor stream with the initial aqueous sulfuric acid solution feed may be done before or after any precooling step.

## THE CLAIMED INVENTION IS:

1. A method of purifying an aqueous sulfuric acid solution comprising the steps of:  
cooling an aqueous sulfuric acid solution to a temperature at or near its freezing point to form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region; and  
separating the acid-rich region from the acid-poor region on the basis of density.
2. A method of claim 1, wherein the separation step comprises the steps of centrifuging the slurry to separate the acid-rich region from the acid-poor region and removing a portion of the acid-rich region from the slurry.
3. A method of claim 2, wherein the separation step further comprises the steps of:  
feeding the remaining slurry to a density column;  
allowing the remaining slurry to form at least one acid-poor region and one acid-rich region on the basis of density;  
removing the acid-rich region from the density column; and  
removing the acid-poor region from the density column.
4. A method of claim 1, wherein the method is a continuous process and wherein the cooling step comprises the steps of:  
precooling the aqueous sulfuric acid solution in a precooling heat exchanger to a temperature above its freezing point;  
removing any precipitated solids from the pre-cooled sulfuric acid solution; and

feeding the precooled sulfuric acid solution to another heat exchanger to cool the pre-cooled sulfuric acid solution to a temperature at or near its freezing point and form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region.

5. A method of claim 4, further comprising the step of combining at least a portion of the removed acid-rich region with the aqueous sulfuric acid solution.

6. A method of claim 1, wherein the separation step further comprises the steps of:

feeding the slurry to a density column,  
allowing the slurry to form at least one acid-rich region and at least one acid-poor region on the basis of density;  
removing the acid-rich region from the density column; and  
removing the acid-poor region from the density column.

7. A method of claim 6, wherein the method is a continuous process and wherein the cooling step comprises the steps of:

precooling the aqueous sulfuric acid solution to a temperature above its freezing point;  
removing any precipitated solids from the pre-cooled sulfuric acid solution; and  
feeding the precooled aqueous sulfuric acid solution to another heat exchanger to cool the pre-cooled sulfuric acid solution to a temperature at or near its freezing point and form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region.

8. A method of claim 1, wherein the method is a continuous process comprising, prior to the cooling step, the step of:

mixing a portion of the separated acid-rich region or of the acid-poor region with the aqueous sulfuric acid solution.

9. A method of claim 1, wherein the sulfuric acid concentration of the aqueous sulfuric acid solution ranges from about 10 to 30% or from about 45 to 95% by weight.

10. A method of claim 1, wherein the aqueous sulfuric acid solution further comprises acids other than sulfuric acid.

11. A method of claim 10, wherein the aqueous sulfuric acid solution further comprises nitric acid or hydrochloric acid or mixtures thereof.

12. A method of claim 1, wherein cooling step occurs in a scraped surface freeze crystallizer.

13. A method of claim 1, wherein the concentration of the aqueous sulfuric acid solution is enriched.

14. A purified aqueous sulfuric acid solution comprising the acid-rich product formed by the process of claim 1.

15. A method of purifying an aqueous sulfuric acid solution comprising the steps of:

cooling an aqueous sulfuric acid solution comprising 10-95% by weight sulfuric acid to at or near its freezing point to form a mixture of a solid phase and a liquid phase in a scraped surface freeze crystallizer;

scraping the solid phase from the freeze crystallizer to form a solid-liquid slurry, the slurry having an acid-rich region and an acid-poor region;  
removing the slurry from the freeze crystallizer; and  
separating the acid-rich region from the acid-poor region on the basis of density.

16. A method of claim 15, wherein the concentration of the aqueous sulfuric acid solution is enriched.

17. A purified aqueous sulfuric acid solution comprising the acid-rich product formed by the process of claim 15.

18. A method of claim 15, the step of separating the acid-rich region from the acid-poor region on the basis of density in at least one of a density column and a centrifuge.

19. A method of purifying a spent aqueous sulfuric acid solution from an industrial process comprising the steps of:

cooling the spent aqueous sulfuric acid solution to a temperature at or near its freezing point to form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region;

separating the acid-rich region from the acid-poor region on the basis of density; and  
recycling the acid-rich region to the industrial process.

20. A method of claim 18, the step of separating the acid-rich region from the acid-poor region on the basis of density in at least one of a density column and a centrifuge.

21. A method of purifying a sulfuric acid solution comprising the steps of:

cooling a sulfuric acid solution to a temperature at or near its freezing point to form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region; and

separating the acid-rich region from the acid-poor region on the basis of density.

22. A method of claim 21, wherein the separation step comprises the steps of centrifuging the slurry to separate the acid-rich region from the acid-poor region and removing a portion of the acid-rich region from the slurry.

23. A method of claim 22, wherein the separation step further comprises the steps of:

feeding the slurry to a density column,

allowing the slurry to form at least one acid-rich region and at least one acid-poor region on the basis of density;

removing the acid-rich region from the density column; and

removing the acid-poor region from the density column.

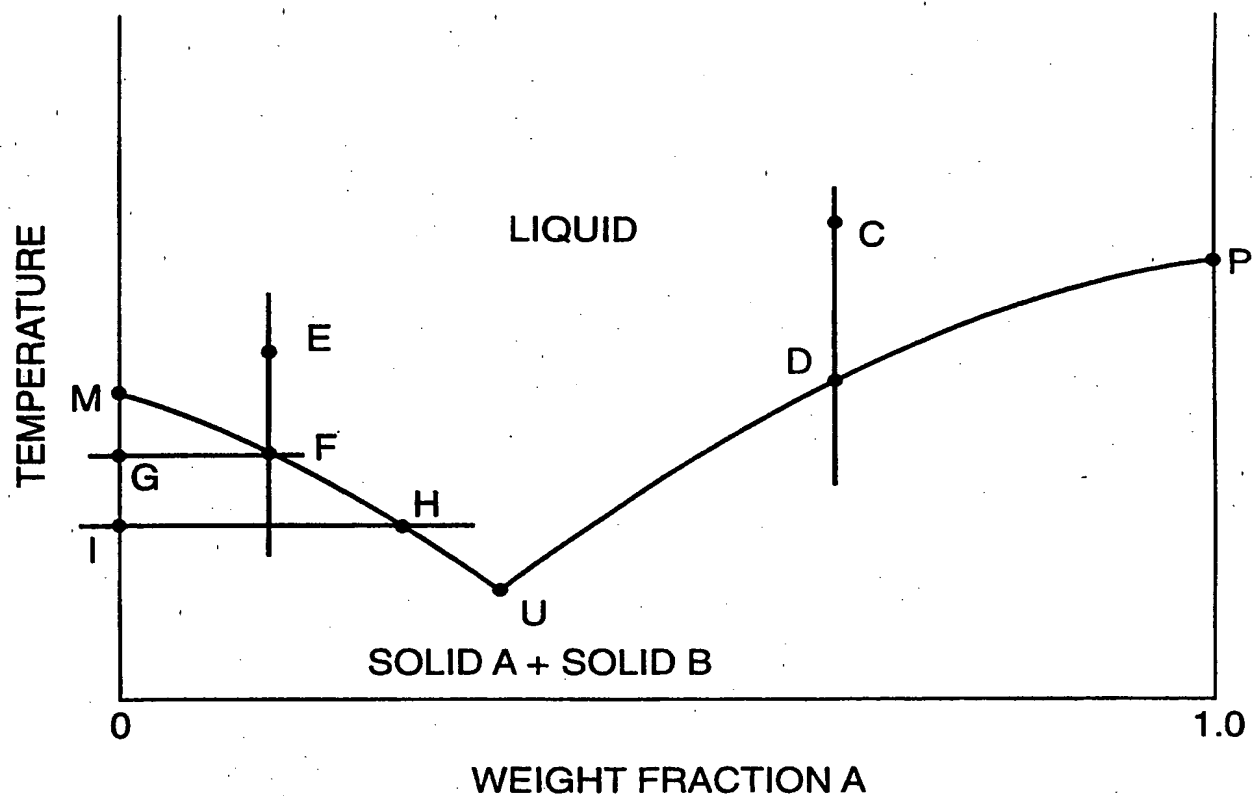
24. A method of claim 23, wherein the method is a continuous process and wherein the cooling step comprises the steps of:

precooling the sulfuric acid solution to a temperature above its freezing point;

removing any precipitated solids from the pre-cooled sulfuric acid solution; and

feeding the precooled sulfuric acid solution to a heat exchanger to cool the pre-cooled sulfuric acid solution to a temperature at or near its freezing point and form a slurry of a solid phase and a liquid phase having an acid-rich region and an acid-poor region.

1/3

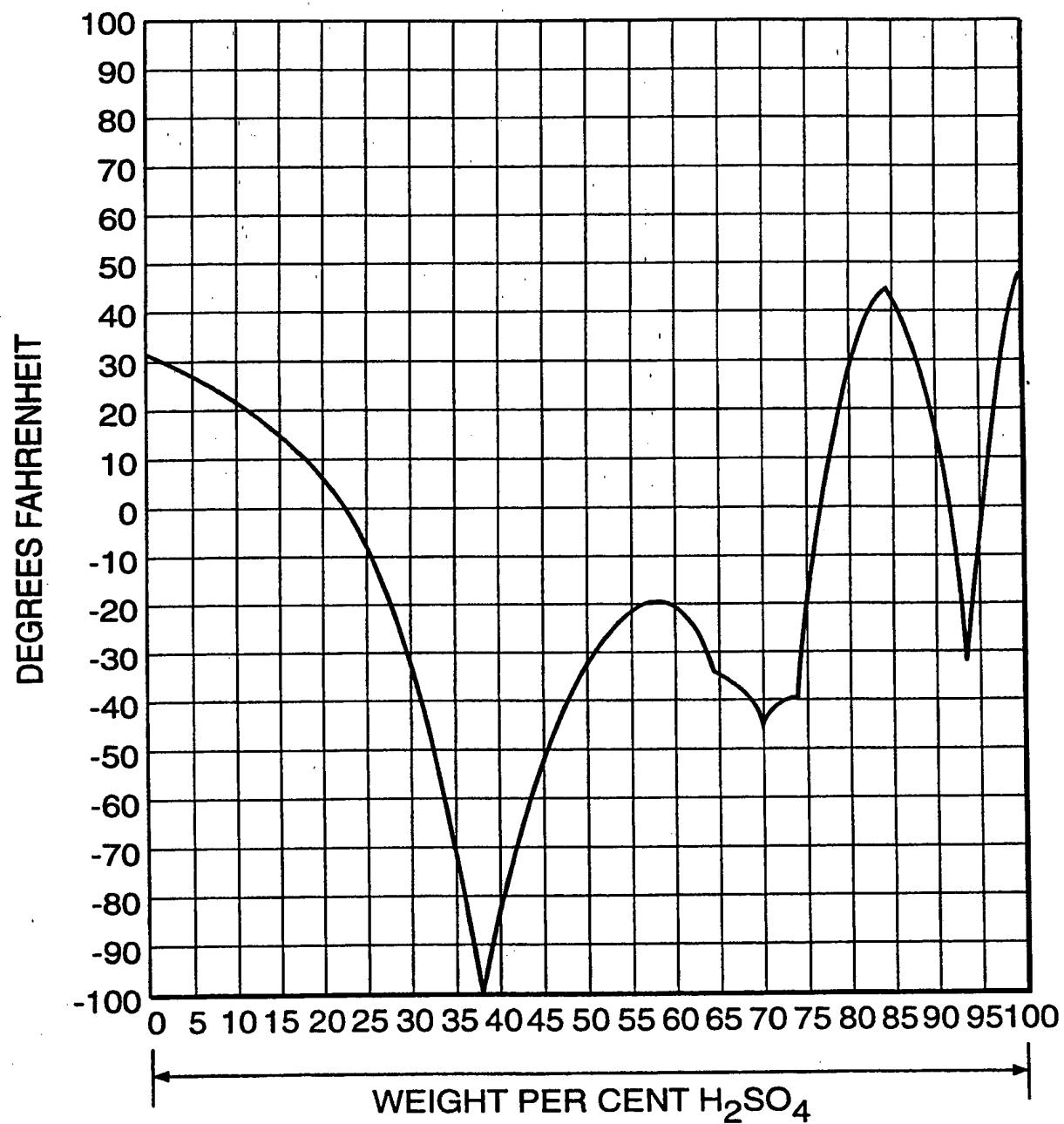
**FIG. 1**

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2/3

## FREEZING POINTS

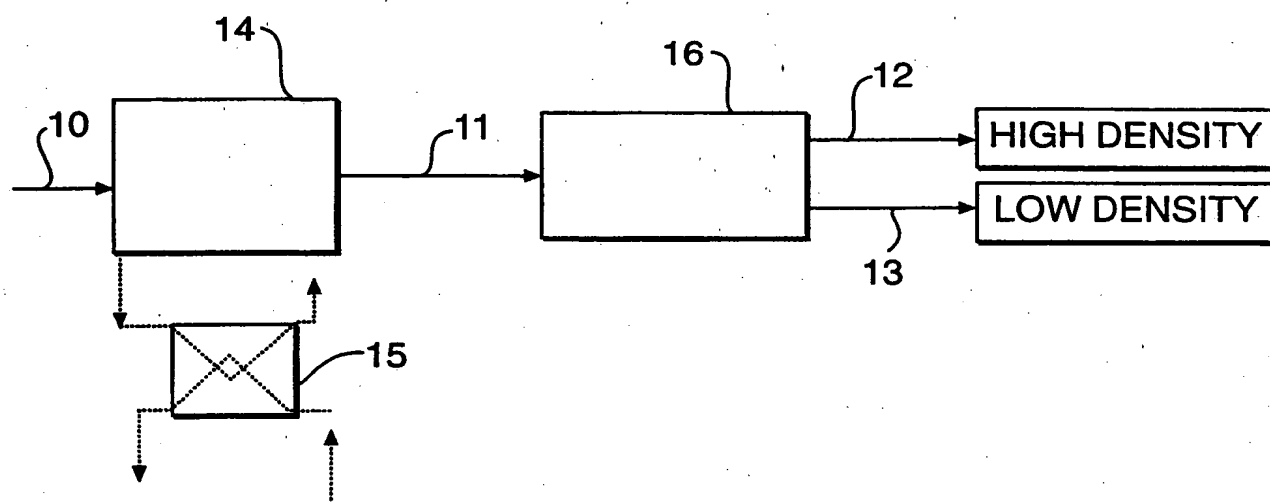
## SULFURIC ACID

**FIG. 2**

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3/3

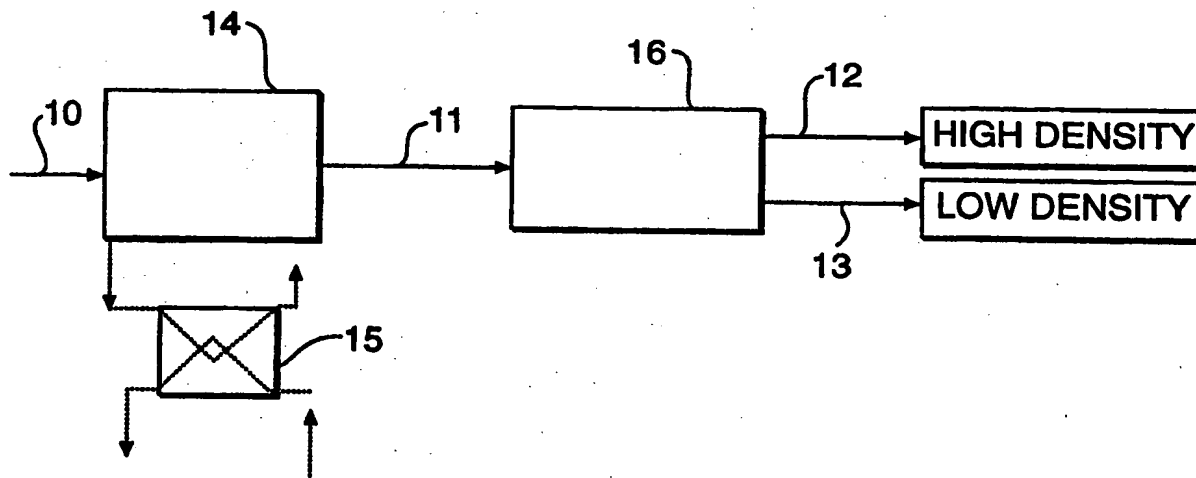
**FIG. 3**





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/06400  <b>(22) International Filing Date:</b> 31 March 1998 (31.03.98)  <b>(30) Priority Data:</b> 08/831,337                      31 March 1997 (31.03.97)                      US  <b>(71) Applicant:</b> WATERWORKS INTERNATIONAL, INC. [US/US]; 130 Commerce Way, Woburn, MA 01801 (US).  <b>(72) Inventors:</b> CONANT, Lawrence, D.; 57 Grant Street, West Bridgewater, MA 02379 (US). KEUS, Arie; 66 Manning Road, Lynn, MA 01902 (US).  <b>(74) Agents:</b> MEYER, Richard, S. et al.; Morgan Lewis & Bockius LLP, 1800 M Street, N.W., Washington, DC 20036-5869 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>  <b>(88) Date of publication of the international search report:</b> 15 April 1999 (15.04.99)

**(54) Title:** SULFURIC ACID PURIFICATION PROCESS**(57) Abstract**

A process for purifying an aqueous sulfuric acid solution includes cooling an aqueous sulfuric acid solution to at or near its freezing point to form a slurry of a solid phase and a liquid phase. The slurry has an acid-rich region and an acid-poor region. The acid-rich region is separated from the acid-poor region on the basis of density.

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# INTERNATIONAL SEARCH REPORT

Int. National Application No  
PCT/US 98/06400

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B17/90

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 862 791 A (STILES) 2 December 1958	1-3, 5-7, 9, 14, 17, 19-24
Y	see the whole document	12, 15, 16, 18
X	GB 796 343 A (KELLOGG) see the whole document	21-23
Y	US 5 394 706 A (KEUS ARIE) 7 March 1995 cited in the application see the whole document	12, 15, 16, 18
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A	DATABASE WPI Section Ch, Week 7802 Derwent Publications Ltd., London, GB; Class E36, AN 78-03058A XP002090284 & JP 52 140497 A (NIPPON MINING CO) , 24 November 1977 see abstract	1
A	US 3 890 097 A (MINOR JOHN T) 17 June 1975	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/06400

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2862791	A	02-12-1958	NONE	
GB 796343	A		NONE	
US 5394706	A	07-03-1995	US 5575160 A US 5537832 A	19-11-1996 23-07-1996
US 3890097	A	17-06-1975	NONE	

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